

Polymer Mass and Thermal Diffusion at a Consolute Critical Point and in the Vicinity of the Glass Transition

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Diffusive flows of matter in polymer solutions and blends can be induced by both a concentration and a temperature gradient. The strength of either flow is determined by the mutual mass diffusion coefficient and the thermal diffusion coefficient, respectively. Mass diffusion slows down dramatically at a consolute critical point, whereas the thermal diffusion coefficient retains its constant background value. As a consequence, the Soret coefficient diverges. The situation is completely different at the glass transition, where the increasing friction slows down both mass and thermal diffusion such that the Soret coefficient of polymer solutions follows power law scaling from semidilute to concentrated and is completely insensitive to the dramatic increase of friction at the glass transition. Both mass and thermal diffusion coefficient are governed by the same microscopic friction coefficient, irrespective whether the glassy state is entered via an increase of polymer concentration at constant temperature or via a decrease of temperature at constant composition. Experimental results are presented for polystyrene/toluene solutions from dilute to concentrated and for blends of poly(dimethyl siloxane) (PDMS) and poly(ethyl-methyl siloxane) (PEMS). The experimental techniques employed are transient holographic gratings and photon correlation spectroscopy.